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## SUBSTITUTION OF ZINC FOR MAGNESIUM.

AND ON A

### RAISED BEACH AT TRAMORE.

[Extracted from the Geological Magazine, May, 1874.]

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#### ON THE SUBSTITUTION OF ZINC FOR MAGNESIUM IN MINERALS.

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N the Geological Magazine of last October<sup>2</sup> I have noticed the occurrence of zinc in small quantities in the White Limestone (Chalk) of the Co. Tyrone, and also in the overlying basalt. When that paper was read.3 exception was taken to the latter part of it, on the ground that the metal in question had never been known to exist in rocks of igneous origin; but as my analysis seemed perfectly trustworthy, I saw no reason to modify it on the objections then put forward. Since then, whilst making an investigationwith a different object-on a specimen of basalt from another locality in the neighbourhood of that whence the one originally examined was obtained, I succeeded in again finding zinc in it; and I think it well to mention the fact now, as an addendum to, and as con-

firming my former statement.

The specimen was procured at a place called Curglasson, near Stewartstown, from the heart of a quarry by the roadside; being more than a mile north of the spot whence the basalt referred to in my former communication was obtained. The rock was carefully examined qualitatively for all the metals precipitable from an acid solution by sulphuretted hydrogen. Iron and alumina were then precipitated, and the filtrate examined with the utmost caution. the addition of ammonium sulphide, a distinct white precipitate appeared. As it was probable that a little lime might have been brought down by a trace of carbonic acid in the re-agents, the precipitate was filtered off, re-dissolved in hydrochloric acid, and reprecipitated. (a) It was again re-dissolved, evaporated to dryness, and strongly ignited, to drive off ammonia, etc. A small quantity of the residue, which was deliquescent, was mixed with carbonate of soda, and exposed before the blowpipe on charcoal. The support became covered with the usual zinc oxide incrustation, which, treated with nitrate of cobalt, gave a vivid green. The fused bead and support were levigated with water in an agate mortar, when numerous spangles of white metal were seen, which, when treated with a drop of water very slightly acidulated with hydrochloric acid, dissolved with evolution of hydrogen. As the solution (a) could only contain zine, with a trace of ferrous iron, and of lime, this experiment was conclusive.

<sup>1</sup> This paper formed part of a communication read before the Royal Irish Academy. <sup>2</sup> Vol. X. page 434. Before the Royal Geological Society of Ireland, June 11, 1873.

The above results were obtained with separate portions of the rock, treated in the following different ways :-

(1). The powdered rock was fused in a platinum crucible with

carbonate of soda.

(2). The powdered rock was boiled in strong hydrochloric acid. (3). The powdered rock was boiled in nitro-hydrochloric acid.

It is somewhat remarkable that only a trace of titanium was

observed in this specimen.

In my former note on this subject, I endeavoured to account for the presence of zinc by the supposition that it existed as a distinct mineral, and pointed out the possibility of its being introduced by the infiltration of water; but subsequent examination and consideration has led me to what appears to be the true clue. Zinc is very closely allied to magnesium in characteristics and behaviour, both in the metallic state and in combination with other elements. In many points the resemblance is very strong; their salts have a similar composition, and these, as well as the natural compounds, or minerals, are isomorphous.2 Consequently, following the law of isomorphism, they should be mutually replaceable; and wherever we find the one in any quantity, we should expect to find the other encroaching on it. It is curious that while in most mineralogical treatises the interchangeability of the protoxides of iron, manganese, calcium, and magnesium is laid down, that of zinc with these, so far as I am aware, has not been yet shown,3 and in the very few instances in which zinc is given as an accessory metal, its presence seems to be considered rather as an accidental circumstance, than as the result of any chemical law. In few cases has it been given in the composition of a mineral, unless when present in such quantity as to make a very serious item in the analyses, as in those of Automolite, or zinc spinel (20 to 35 per cent. of Zn 0), and Franklinite (17 per cent. Zn 0); while in most minerals traces of Mn, Fe, Mg, are constantly recorded as replacing part of the essential metals.

Believing, therefore, that zinc compounds might thus be calculated to occur in most magnesian rocks or minerals, I have tried several, and so far the result has almost exceeded my expectations, for in every single case the metal was proved. As yet I have merely satisfied myself with regard to its presence, reserving the quantitative determination until I shall have completed the testing of a number of specimens; but it may he worth while to mention the rocks and

minerals already searched.

1. Granite.—Wicklow and Wexford range variety: from Graiguena-spiddoge, near Carlow.—Obtained from heart of quarry: (a) A very coarse-grained light grey rock, porphyritic in parts, containing white mica, together with a dark greenish magnesian variety; also tourmaline. The portion taken for analysis was prepared in such a

nalysis, p. 49.

2 Supra cit.; also Dana's Manual of Mineralogy, p. 74.

4 Leinster Granite. 3 Although in one or two cases implied.

<sup>&</sup>lt;sup>1</sup> Fownes' Manual of Chemistry, 10th ed. p. 393; also Galloway's Qualitative Analysis, p. 49.

way as to contain a preponderance of mica, and four analyses of this were made in the wet, as well as others in the dry, way, ere I allowed myself to be perfectly satisfied as to the presence of zinc. The quantity of this was very small, as was of course to be expected.

Traces of copper and lead were also noticed.

(b.) Mica.—After many searches at the same quarry, I was fortunate enough to find a mass of mica sufficiently large for analysis with the blowpipe. It was mostly white, but contained lamine of green mica. About four grains were treated on charcoal before the blowpipe, with carbonate of soda. Two metals were reduced, which proved to be copper and zinc. The zinc spangles dissolved with rapid evolution of hydrogen in a barely acid solution of hydrochloric acid. The solution evaporated to dryness, moistened with nitrate of cobalt, and heated on charcoal, gave the characteristic green reaction.<sup>1</sup>

2. Serpentine (?).—A green soft steatitic rock from Garrarus Strand, near Tramore, Co. Waterford. This rock occurs among Silurian limestones and slates, near masses and dykes of felstone, etc. Some of the limestone can be distinctly seen to pass into Serpentine. Examined qualitatively for zinc: found it present in fair quantity, all the re-actions being most distinct.

This rock contains about 8 per cent. of water, and 11 per cent.

of carbonic acid (CO<sub>2</sub>).2

3. Basalt.—Already described.

4. Black Mica.—In a gneissose or granitic rock. Locality unknown. Specimen from Geological Survey collection.<sup>3</sup> The mica is perfectly black, and occurs in quantity in small flakes thickly massed together.

About four grains were treated at a time before the blowpipe with carbonate of soda. After fusion the mass yielded a notable quantity of copper, a very appreciable amount of zinc, and a trace of a metal which seemed to be lead. All the characteristic tests for

zinc were answered very distinctly.

5. Chlorite schist (? Tale schist).—With inclosed grains of glauconite (?). From Geological Survey Collection. The examination with the blowpipe gave two metals, both in very appreciable quantity, viz. copper and zinc. The zinc re-actions were very pronounced.

6. "Mountain Leather."—Variety of asbestus. From Portlock's Collection, Geological Survey Museum, Dublin. Locality unknown; but associated with asbestus and other basaltic minerals from Antrim. Zinc very apparent, all the re-actions being perfectly unmistakable.

A trace of lead (?) was also observed.

7. Augite.—Very large crystals in a trappean ash. Locality unknown. From Geological Survey Collection. About four or five grains of the powdered mineral, fused with carbonate of soda on

<sup>3</sup> The specimens from the Survey Collection were obtained by the kind permission of Prof. Hull, F.R.S., Director of the Geological Survey of Ireland.

The zinc most probably occurs here in the dark magnesian mica.
 It is therefore not entirely metamorphosed.

charcoal, yielded a sufficiency of metal to identify with certainty. Besides zinc, copper was present. All the zinc re-actions were most distinct.

All the above minerals and rocks were selected at random, on account of containing, or being themselves, magnesian compounds, and they are numbered in the order in which they were examined, every one resulting in "a find." In many cases the examination by the blowpipe and its immediately connected wet tests was found to be amply sufficient to prove the presence of the metal; especially as from the comparatively large amount of the substance under investigation taken,—four or five grains,!—there was little possibility of error. But where the result was at all doubtful, it was confirmed by one or more analyses in the wet way.

The amount of zinc appeared to be most plentiful where the largest quantity of magnesium existed; but as I am as yet only concerned in proving the presence of the former metal in the above minerals, I am not now in a position to positively assert this; deferring the quantitative analyses until I have continued the investigation so far as to enable me to select the most typical examples for estimation. In the mean time these notes on the subject may not be without some interest, bearing as they do on a matter of much importance from a mineralogical as well as a chemical standpoint.

It may be thought that the zinc might as well be considered to replace the other members of the isomorphous group, which are known to occur in traces and occasionally in quantity in some of these minerals. But this would be a replacement of a replacing element; and I believe it is invariably considered that the accessory metal substitutes itself for part of the essential one. On this ground alone, all the minerals here referred to being strictly magnesian ones, the zinc must be regarded as replacing magnesium. At the same time I do not doubt that in other instances where there is no magnesium, it may be equally found to replace any of the other members. But when we remember the affinities of the two metals, it will hardly be considered a far-fetched notion to suppose, that were a preference possible, the zinc would associate itself with the magnesium, in the same way as some other metals act towards each other, notably the Platinic group; which possessing a very peculiar relation to one another independently of their isomorphism-which is not thorough -are nearly always found together.

It will be seen that the majority of the minerals examined are species that are most often found in nature forming component parts of igneous rocks, while two rocks of that class are themselves in-

cluded.

<sup>&</sup>lt;sup>1</sup> This was rendered possible by the use of paraffin oil in the blowpipe lamp, by which a very large and hot flame was procured, capable of decomposing a much larger quantity of rock. For reductions, and where great heat is required in blowpipe analysis, it will be found most useful where gas is unattainable.

# TRAMORE. BEACH AT RAISED

VERTICAL SECTIONS.

F16. 4.



The numbers 1, 2, 3, . . . are intended to show the correlation of the different beds.

FIG. 5. SECTION ALONG SHORE AT LISSELLAN.

SCALE.—Longitudinal: 12 in. = one mile. Vertical: 1 in. = 36 feet.

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- Dark Peaty sandy layer. Shells abundant at base ...... Upper Gravel bed, with a few shells
  - Lower Gravel Bed; Curved Stratification. Shells very abundant. Blue mud layer, extending into cracks in (1)...... Gravelly Brown Boulder-clay, eroded ...... 964.891

1st Land Surface.

1st Depression.



[Extracted from the Geological Magazine, Decade II., Vol. I., No. 5, May, 1874.]

NOTE ON A SMALL RAISED ESTUARINE BEACH AT TRAMORE BAY, CO. WATERFORD, SHOWING TRACES OF SEVERAL OSCILLATORY MOVEMENTS DURING THE RECENT PERIOD.

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#### (PLATE XI.)

WHILE spending a few days in the Autumn at Tramore, I chanced to meet with a well-marked example of recent alteration of shore-level; and as on subsequent examination I find it only partially noticed on the Six-inch Map, and not referred to at all on the published One-inch Sheet, or in the Memoir of the Geological Survey of the District, I thought of laying a short note on the subject before this Society.

The Bay of Tramore is separated by a long ridge of sand-hills known as the Burrow—chiefly of aërial origin—from an extensive muddy estuarine flat called the Backstrand, the result of the silt of

<sup>&</sup>lt;sup>1</sup> Read before the Royal Geological Society of Ireland, December 9, 1873.

two or three streams flowing into and through it, at present of trifling size, but which must formerly have been of some importance as mud-carriers, as is shown by the dimensions of the old river-courses now filled by alluvium. These streams coalesce into one, that finds its way to the sea by a narrow passage called the Rinnashark. At various places around the estuary, and at heights varying from two to ten feet above high-water mark, layers of sand, clay, and gravel are found, resting on Boulder-clay, vegetable soil, or-as in one place—a thick layer of good peat bog; and containing numerous specimens of recent marine shells, chiefly the common cockle,-Cardium edule,—with Turritella, Littorina, Modiola, etc. Time did not permit of my making a very careful examination of the fossil contents of these beds. I was, however, able to trace the Raised Beach for about a mile on each side of the estuary. On the east side it is very well marked indeed as to configuration, forming a narrow stretch of low flat ground along the margin of the shore, and with shells tolerably abundant, these being also found at some little distance from the shore, in the sides of a ditch a field off. on the west only a few isolated patches of shelly gravel were to be found; and the shape of the shore is not such as to suggest the existence of a raised beach. Yet of this there can be no question, as will be seen from the following details.

The first section seen on the west, at the north-eastern junction of Crobally Upper with Crobally Lower, and near the former mouth

of one of the streams flowing into the bay, is as follows:

_	(See Plate XI. Fig. 1, p. 214.) Mould, clay, etc. (artificial)	Ft.	In.	Ft. I	n.
b.	Stratified sand containing fragments and whole shells of Cardium	-	,		
	edule, Turritella, etc	2	0 }	10	0
a.	Boulder-clay, with Talus of recent sand, etc., in all	8	0)		

The shelly bed here is somewhat variable in thickness—from six inches to two feet—and in level; but its height above present high-

water mark is about ten feet.

Crossing the stream, and proceeding northwards along the coast for about 600 yards, we come to a place marked on the working Sixinch Map with the following note by Mr. W. L. Willson, who examined this district in the early days of the Survey:—"Layers of Cockle-shells (in sitú) 2½ feet above present level of high-water, imbedded whole as if buried alive, in clayey drift." I could not find the deposit here alluded to, as it has been "improved off the face of the earth"; but a little to the east of the spot, in a new drain running from a sluice gate in the recently built Reclamation Wall, crossing the estuary from this point, I saw the following remarkable section (see Plate XI. Fig. 2, p. 214):—

				rt. I	ш,
e.	Clayey bed with broken Cockle-shells, about			0	8
d.	Brown solid Peat			2	0
c.	Clavey brown Sand			2	0
a.	b. Brown clavey Boulder-clay, with cracks or pipes filled with	blue	stiff		
	clay, to water's edge			1	0
	¥,				_
				-	0

The Cockle-bed was at a height of from two to three feet above high-water mark. Had I not seen other sections having a direct bearing on the above, and of some if not entire similarity to it, I should have been inclined to reject bed e as of artificial origin: but, as the sequel will show, there is a strong presumption that it is really in sitů. In a drain along a new road, being the continuation of the wall to the westward, a somewhat similar section is seen:

(See Plate XI. Fig. 3, p. 214.)						
d. Soil, etc		1 6				
c. Peaty layer, becoming sandy inland		1 0				
b. Bluish mud containing fragments of wood		1 6				
a. Sandy Boulder-clay, with cracks filled up with blue mud		4 0				

The shells are absent here, possibly because the former submergence did not extend so far. The peaty layer undoubtedly corresponds with the boggy bed of the last section.

Five hundred yards north of the sluice-gate, and close to the division of the Townlands, Ballinatin, and Drumcannon, Mr. Willson has noted "Layers of Cockle-shells 2½ feet above high-water mark."

This has also disappeared.

The foregoing are the only traces to be found on the west of the estuary; but on crossing the Reclamation Dyke to the other side, the old beach becomes very apparent, and a little to the north, about sixty yards from high-water mark, an excellent section is seen (See Plate XI. Fig. 4, p. 214):

	Section in Lissellan.	Ft	Īn.	E+	. In.
d.	Vegetable soil and clay			- 0	
c.	Dark sandy layer, rather peaty, containing abundantly at base				
	layers of shells, Cockle, Mussel, Winkle, etc	0	3	to 0	6
	Muddy layer, thin and irregular, in pockets	0	2		
<i>a</i> .	Gravelly brown Boulder-clay with irregular cracks containing blue				
	mud strings	6	0	to 9	0
		7	5	to 9	6

The height of the shell-bed is here about nine or ten feet above high-water mark, and it is found extending inland in a section exposed in a ditch, continuing into the next field.

A little south of this, and close to high-water mark, the same section is seen; but here bed c. becomes very-black, from the presence of organic matter, in some places very peaty, and thickens to one foot. Bed b. is sometimes a foot thick, and the height of the shell-bed is

seven feet above high water mark.

Continuing southwards in Lissellan, the peaty layer is underlaid by a few thin layers of well-stratified gravel, full of shells, which die out after a little distance. Further on along the shore the level of the peaty bed sinks gradually, and at last is covered by a distinct layer of rudely-stratified gravel, in which a few shells are found, being evidently a shore deposit. This, which is about a foot thick. and is covered with mould well clothed with grass, continues for nearly half a mile, the height diminishing to about two feet, until it

gradually disappears under a thin bog connected with an alluvial flat. (See Plate XI. Fig. 5, p. 214.) This bog is itself covered by

high-water of spring-tides.

I think there is sufficient resemblance between these sections and Figs. 2 and 3, to warrant us in referring them all to one horizon, and in believing the shells above the peat in Fig. 2 to be in sitů, corresponding to the gravel-bed above the black bed in Lissellan.

North of the Wall (or of Section 4) the raised beach can be traced for about half a mile by its appearance, which is tolerably distinct.

It seems to die out towards the head of the estuary.

Although this beach is of insignificant extent, it is of some interest on account of its recording several oscillations of surface as having occurred during Post-Glacial times; for it will be observed that from the sections three distinct land-surfaces and as many silt-beds can be identified. First and lowest comes the Boulder-clay, evidently dennded, perhaps after depression, and a deposit of mud and gravel, with shells laid on it—First Submergence. Then we have the land rising again, marked by a dark sandy bed full of vegetable matter (? old alluvium), with, in places, shells at the base, becoming in part peat bog—Second Land-Surface. Next comes a deposit of gravel, stratified, and in at least two places containing shells—Second Submergence. This is covered by quite recent bog passing into alluvium along the Keiloge River—Third Land-Surface. And the last is now subject to floods at spring-tides—showing that the Third Submergence has commenced.

With regard to this last, it may be mentioned that at the southwestern corner of the estuary, close to the town, there is a partiallysubmerged and silt-covered bog,1 which appears to be connected with an alluvial flat extending northwards. This bog has been buried for many years, for it was recorded on the Six-inch Working Map by Mr. Willson in the beginning of the Survey. At present there is no trace of it; but during the great storm of 1870 the strand was torn up and the bog laid bare. In the summer of that year I happened to be in the neighbourhood, and visiting the strand saw the bog where it was even then visible between high- and low-water mark. It appeared to have been covered by not more than six inches of sand, and was certainly in sitû, and not the result of a quantity of bog having slipped, and spread over the sand. Had this been so, it must have been levelled and removed by the tidal action long before I saw it. The strand being now re-formed, there is none of the bog visible. It is possible that it is contemporaneous with the alluvial bog referred to above as capping the last gravel-bed in Section 5, at Lissellan; but that either because the land commenced to sink towards the south, or by reason of the slope of the ground, the latter has as yet only barely come within the influence of the

The subject of changes of level in estuaries as shown by the presence of alternating beds of peat or vegetable soil and silt, etc.,

<sup>1</sup> The strand under which it lies is covered totally at high-water.

has been well treated by Mr. T. Mellard Reade, F.G.S., in an elaborate and exhaustive paper on the Estuaries of the Mersey, Dee, and Ribble, in which he has made out from three to four distinct periods of submergence and upheaval, and he insists on the frequency of such movements. This idea seems to me to be well borne out by the number of sea and land surfaces shown in such a trifling thickness of strata as at Tramore. At the same time, we must remember that extensive denudation might have taken place between each deposit, although this is not denoted by what is going on there at present, since we see one part of the bog submerged and silted over, while the other is still growing.

With regard to other parts of our own coasts, I have no doubt that the same phenomena have been also observed; but I have no opportunity of verifying this at present. However, the shelly gravel of Dundalk 2 may possibly be due to something of the same nature, and this is undoubtedly true in the case of the remarkable shell and peat deposit underlying Belfast:3 while another instance in the South of Ireland is furnished by the Estuary of Wexford, of which, through the kindness of G. H. Kinahan, Esq., M.R.I.A., I am in possession of some details showing that recent oscillations have been going on there to a great extent. Around the coast, submerged bog is common, and in the Estuary itself the following section is noted by him:4-

"North Mudlands, Wexford Estuary, at the Engine House at the ancient island called 'The Ridge.'

						Ft.	In.
4.	Marl		•••	 	 •••	 16	0
3.	Peat			 	 	 5	0
2.	Grev	muddy	stuff	 	 	 1	5
- 1	351						

"The top of the marl, No. 4, is a few fathoms (about four) below average high-water mark. This section was procured while sinking the foundation of the Engine House."

Dub. Geol. Soc. vol. i.

3 Mr. J. Grainger, 22nd Report Brit. Assoc., 1852, p. 42. Also Ex. pl. Memoir (Sheet 36), Geol. Survey, Ireland, p. 38. 4 MS, note.

Post-glacial Geology of Lancashire and Cheshire, by T. Mellard Reade, C.E., F.G.S., etc., Proc. Liverpool Geol. Soc., November, 1871. An instance of blue mud penetrating into cracks in the Boulder-clay beneath is noted (p. 45, Detailed Sections), just as in the Sections given above. (See Geor. Mac. 1872, Vol. 1X. p. 111.)

2 On the Shelly Gravel underlying Dundalk, by Gen. Portlock, F.R.S., etc., Journ.









